Methods for Predicting the Thermal Conductivity of Composite Systems: A Review

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The thermal conductivity of a solid or gas filled polymer is used in processing or end use application calculations. Numerous theoretical and empirical correlations are found in the literature. A careful review of these models indictes that no one correlation or technique accurately predicts the thermal conductivity of all types of composites. The investigation indicated that for solid filled composites the Lewis and Nielsen equation fitted the experimental data best for the range of fillers tested. However, for a gas filled polymer, none of the theoretical models proved adequate. The semi-empirical approach of Harding showed considerable merit.

INTRODUCTION

Throughout this review article a composite is defined as "a substance formed from one or more discrete components imbedded in a homogeneous, *continuous*, stationary medium". Specifically, our discussion is limited to finite particles and/or gas filled voids imbedded in a medium. A group of discrete particles in intimate contact or particles in a stationary or moving air matrix are not considered to be composites. Early in the investigation an attempt was made to classify all available references found in the literature into solid-solid and gas-solid compositions. However, it was apparent that the theoretical models were used by numerous authors for both types of systems. We, therefore, present herein many of the various theoretical and empirical models and provide a brief description of the basis for each in our literature review section. Discussion and comments are presented in the section entitled General Discussion.

LITERATURE REVIEW

Listed alphabetically in the Bibliography are a group of papers associated with the energy transfer and/or gas diffusion in a filled composite. In this section are listed several theoretical or empirical models and a brief description of their basis. Our literature review encompassed a considerable amount of material but in no way should it be assumed complete. The following general nomenclature is used in the paper:

k_c = thermal conductivity of continuous phase
k_d = thermal conductivity of discrete phase
k_i = thermal conductivity of one of the discrete phases
k_e, k_x, k_y = thermal conductivity of composite
ϕ = volume fraction of discrete phase
x = parallel to filament axis
y = perpendicular to filament axis

Coefficients and other symbols unique to individual models will be identified when the model is analyzed.

Series Model:

$$k_e = (1 - \phi)k_c + \phi k_d \qquad (1)$$

Parallel Model:

$$\frac{1}{k_e} = \frac{1 - \phi}{k_c} + \frac{\phi}{k_d} \qquad (2)$$

Geometric Mean Model:

$$k_e = k_d{}^{\phi} k_c{}^{(1-\phi)} \qquad (3)$$

Behrens Theoretical Model (6)

The theoretical results were based on a field solution to the equation of heat conduction for a composite material with orthorhombic symmetry. Solutions were presented for elliptic filaments in a square lattice:

$$\frac{k_x}{k_c} = 1 + (p-1)\phi - (p-1)^2$$

$$\frac{\sigma - \frac{\epsilon^2}{2}}{1 - \epsilon^2}\left[\frac{(1 - \epsilon^2)\phi - \left(\sigma - \frac{\epsilon^2}{2}\right)}{(p+1)\frac{\epsilon^2}{2} - (p-1)(\phi - \sigma)}\right] \quad (4)$$

$$\frac{k_y}{k_c} = 1 + \frac{(p-1)\phi\epsilon^2}{(p+1)\frac{\epsilon^2}{2} - (p-1)(\phi - \sigma)} \quad (5)$$

where $p = \dfrac{k_d}{k_c}$

$$\sigma = \sqrt{\frac{\epsilon^4}{4} + (1 - \epsilon^2)\phi^2}$$

$$\epsilon = \frac{\text{Major axis of ellipsoid}}{\text{Focal distance}}$$

For circular rods this reduces to:

$$k_e = k_c\left[\frac{(p+1) + (p-1)\phi}{(p+1) - (p-1)\phi}\right] \quad (6)$$

And for cubic symmetry of spheres:

$$k_c = k_c\left[\frac{(p+2) + (p-1)2\phi}{(p+2) - (p-1)\phi}\right] \quad (7)$$

which reduces to Maxwell's equation.

Bruggeman Theoretical Model (7)

Using different assumptions than Maxwell for permeability and field strength, Bruggeman derived the following implicit equation for dilute suspensions of spheres in a homogeneous medium:

$$1 - \phi = \left[\frac{k_d - k_e}{k_d - k_c}\right]\left(\frac{k_c}{k_e}\right)^{1/3} \quad (8)$$

Budiansky Theoretical Model (9)

Budiansky established an analogy between an electrostatic field and temperature distribution in a composite consisting of a random mixture of N isotropic constituents, at least $(N - 1)$ of which are presumed to be roughly spherical in shape. The conductivity can be extracted from the following implicit equation:

$$\sum_{i=1}^{n}\frac{\phi_i}{\frac{2}{3} + \frac{1}{3}\frac{k_i}{k_c}} = 1 \quad (9)$$

Cheng and Vachon Theoretical Model (12)

Starting with Tsao's basic probablistic model, Cheng and Vachon assumed the discontinuous phase had a parabolic distribution. Based upon this assumed distribution, Tsao's constants were evaluated and a closed form expressions for effective thermal conductivity of a two phase mixture as a function of discontinuous phase volume fraction were obtained:

$$k_c > k_d$$

$$\frac{1}{k_e} = \frac{2}{\sqrt{C(k_d - k_c)[k_c + B(k_d - k_c)]}}\tan^{-1}$$

$$\frac{B}{2}\sqrt{\frac{C(k_d - k_c)}{k_c + B(k_d - k_c)}} + \frac{1 - B}{k_c} \quad (10)$$

$$k_d > k_c$$

$$\frac{1}{k_e} = \frac{1}{\sqrt{C(k_c - k_d)[k_c + B(k_d - k_c)]}}$$

$$\ln\frac{\sqrt{(k_c + B(k_d - k_c))} + \frac{B}{2}\sqrt{C(k_c - k_d)}}{\sqrt{k_c + B(k_d - k_c)} - \frac{B}{2}\sqrt{C(k_c - k_d)}} + \frac{1 - B}{k_c} \quad (11)$$

where for both equations:

$$B = \sqrt{3\phi/2} \qquad C = -4\sqrt{2/(3\phi)}$$

For three or more phase mixtures a discussion was presented on several techniques that could be used to estimate effective thermal conductivities of the composite.

Donea Variational Model (20)

Using variational principles Donea obtained the upper, k^+, and lower, k^-, bounds for the effective thermal conductivity of a composite material which is statistically homogeneous and contains two phases each having isotropic and uniform thermal conductivity.

$$k^+ = \phi k^- + (1 - \phi)k_c \quad (12)$$

$$k^- = \frac{\hat{k}\,k_c}{k_c + (1 - \phi)\hat{k}} \quad (13)$$

Spheres:

$$\hat{k} = \frac{k_c[(p+2) + 2s(p-1)]}{(p+2) - (p-1)s} \quad (14)$$

where $p = k_d/k_c$, $s = (a/b)^3$, a = radius of inclusion, b = radius of the largest possible spherical shell surrounding the inclusion for random dispersion of spheres, and $k^+ = k^- = \hat{k}$.

Parallel Circular Fibers:

$$k = \frac{k_c[(p+1) + (p-1)s]}{(p+1) - (p-1)s} \quad (15)$$

where $p = k_d/k_c$, $s = (a/b)^2$, a = radius of fiber, and b = radius of largest hollow cylinder surrounding the fiber.

These equations yield the lower bounds. For the case of no geometric constraints with $p > 1$ it has been shown that by reversing the roles of the continuous and discrete conductivities in the above equations form the upper bounds.

Fricke Theoretical Model (24)

Fricke extended Maxwell's analysis to homogeneous ellipsoidal particles that are far apart in a homogeneous medium:

$$k_e = k_c \left\{ \frac{1 + \left[F \frac{k_d}{k_c} - 1 \right]}{1 + \phi(F - 1)} \right\} \qquad (16)$$

where

$$F = \frac{1}{3} \sum_{1}^{3} \left[1 + \left(\frac{k_d}{k_c} - 1 \right) f_i \right]^{-1}$$

and

$$\sum_{i=1}^{3} f_i = 1$$

The factor F represents the ratio of the overall temperature gradients in the two phases and the f_i's the semi-principal axes of the ellipsoid. For a sphere $f_1 = f_2 = f_3$ and the equation reduces to Maxwell's equation.

Halpin-Tsai Theoretical Model (2)

For filaments of uniform cross-sectional area arranged in parallel, the thermal conductivity parallel to the filaments was assumed to be (parallel model):

$$k_e = \phi k_d + (1 - \phi) k_c \qquad (17)$$

Using an analogy between in-plane field equations and boundary conditions to the transverse transport coefficient, the transverse thermal conductivity is:

$$k_e = \frac{1 + \zeta \eta \phi}{1 - \eta \phi}$$

where

$$\eta = \frac{\frac{k_d}{k_c} - 1}{\frac{k_d}{k_c} + \zeta}$$

for plates of width a and thickness b:

$$\zeta = \sqrt{3} \, \log \left(\frac{a}{b} \right)$$

and for circular or square fibers:

$$\zeta = 1.0$$

Hamilton and Crosser Semi-Theoretical Model (28, 29)

Hamilton and Crosser define the thermal conductivity of a two component mixture as:

$$k_e = \frac{k_c(1 - \phi) \left. \frac{dt}{dx} \right|_1 + k_d \phi \left. \frac{dT}{dx} \right|_2}{(1 - \phi) \left. \frac{dt}{dx} \right|_1 + \phi \left. \frac{dT}{dx} \right|_2} \qquad (18)$$

The ratio of thermal gradients can be determined from the theoretical work of Maxwell and Fricke.

$$\frac{\left. \frac{dT}{dx} \right|_d}{\left. \frac{dT}{dx} \right|_c} = \frac{n \, k_c}{k_d + (n - 1)k_c}$$

which substituted into *Eq 18* results in:

$$k_e = k_c \left[\frac{k_d + (n - 1)k_c - (n - 1)\phi(k_c - k_d)}{k_d + (n - 1)k_c + \phi(k_c - k_d)} \right] \qquad (19)$$

where n is an empirical constant. For a spherical particle Maxwell showed analytically that $n = 3.0$. For nonspherical particles Hamilton and Crosser correlated numerous sets of data with $(0.58 < \psi < 1.0)$:

$$n = \frac{3}{\psi}$$

where ψ is the sphericity. The sphericity was defined as the ratio of the surface area of a sphere, with a volume equal to that of the particle, to the surface area of the particles.

In a similar manner the thermal conductivity of a multi-phase mixture was given as:

$$k_e = k_c \frac{\left[1 - \sum_{i=2}^{m} \frac{\phi_i(n_i - 1) \, (k_c - k_i)}{k_i + (n_i - 1)k_i} \right]}{\left[1 + \sum_{i=2}^{m} \frac{\phi_i(k_1 - k_i)}{k_i + (n_i - 1)k_i} \right]} \qquad (20)$$

Harding Semi-Empirical Model (32-36)

Starting with an elementary conduction, convection, and radiation heat transfer analysis for low density, cellular foam, Harding obtained a semi-empirical relationship.

$$\begin{aligned} k_e = \, & k_c E_s (1 - \phi) \\ & + k_d \phi + (k_b - k_a)\phi(1 - F) \, (1 - 0.5 R_g V_g^{1/3})M \\ & + \frac{C_r V_g^{1/3}}{\phi} \left[\frac{T_h + T_c + 920}{1000} \right]^3 \qquad (21) \end{aligned}$$

where E_s = dimensionless efficiency fact for heat conduction through foam solids (empirical), k_a = thermal conductivity of air, k_b = thermal conductivity of blowing agent, R_g = geometric ratio of cut surface exposed per unit foam volume, V_g = volume of gas in average cell, M = mean mole fraction of blowing agent in a cell, and C_r = coefficient defining the rate of radiant energy transfer through foam.

Jefferson, Witzell and Sibbitt Theoretical Model (43)

Jefferson, Witzell, and Sibbitt assuming the particles were spherical in nature devised a series-parallel equivalent system for a singular particle in a cube of continuous medium:

$$k_e = k_c \left[1 - \frac{\pi}{4(1 + 2n)^2} \right] + \frac{\pi}{4(1 + 2n)^2} \left[\frac{(0.5 + n)k_a k_c}{0.5 k_c + n k_a} \right] \qquad (22)$$

where n and k_a are:

$$n = 0.403 \, \phi^{-1/3} - 0.5$$

$$k_a = k_d k_c \left[\frac{2k_d}{(k_d - k_1)^2} \ln \frac{k_d}{k_c} - \frac{2}{(k_d - k_c)} \right] \qquad (23)$$

Lewis and Nielsen Semi-Theoretical Model (53, 59-63)

Lewis and Nielsen modified the Halpin-Tsai equation to include the effect of the shape of the particles and the orientation or type of packing for a two-phase system.

$$k_e = k_c \left[\frac{1 + A\,B\,\phi}{1 - B\,\phi\,\psi} \right] \qquad (24)$$

where

$$A = k_{en} - 1$$

$$B = \frac{\dfrac{k_d}{k_c} - 1}{\dfrac{k_d}{k_c} + A}$$

$$\psi = 1 + \left(\frac{1 - \phi_m}{\phi_m^2} \right)\phi$$

The values of A and ϕ_m for many geometric shapes and orientation are given in the following tables:

Type of dispersed phase	Direction of heat flow	A
Cubes	Any	2.0
Spheres	Any	1.50
Aggregates of spheres	Any	$\dfrac{2.50}{\phi_a} - 1$
Randomly oriented rods Aspect ratio = 2	Any	1.58
Randomly oriented rods Aspect ratio = 4	Any	2.08
Randomly oriented rods Aspect ratio = 6	Any	2.8
Randomly oriented rods Aspect ratio = 10	Any	4.93
Randomly oriented rods Aspect ratio = 15	Any	8.38
Uniaxially oriented fibers	Parallel to fibers	2L/D
Uniaxially oriented fibers	Perpendicular to fibers	0.5

Shape of Particle	Type of Packing	ϕ_m
Spheres	Hexagonal close	0.7405
Spheres	Face centered cubic	0.7405
Spheres	Body centered cubic	0.60
Spheres	Simple cubic	0.524
Spheres	Random close	0.637
Spheres	Random close	0.601
Rods or fibers	Uniaxial hexagonal close	0.907
Rods or fibers	Uniaxial simple cubic	0.785
Rods or fibers	Uniaxial random	0.82
Rods or fibers	Three dimensional random	0.52

The values of A listed in the table are for elastic moduli. In general, the theoretical values for conductivity are slightly greater.

Loeb Theoretical Model (54)

Loeb derived a relationship for the effective thermal conductivity of a porous solid as a function of the cross-sectional and longitudinal pore fractions and surface emissivity.

$$k_e = k_c \left[1 - \phi_c \left(\frac{1 - \dfrac{4\gamma\epsilon\sigma\overline{\Delta T}^3}{k_c}}{1 + \dfrac{4\gamma\epsilon\sigma\overline{\Delta T}^3}{k_c}\left(\dfrac{1 - \phi_1}{\phi_1} \right)} \right) \right] \quad (25)$$

where ϕ = cross-sectional porosity, ϕ_1 = longitudinal porosity, γ = geometrical factor, ϵ = pore emissivity, σ = Stefan-Boltzman constant, and $\overline{\Delta T}$ = temperature difference.

The Loeb model attempts to compensate for radiation in the direction parallel to heat flow. For an orderly array of pores the above model was incorporated with a series-parallel analysis.

Maxwell Theoretical Model (56)

Maxwell using potential theory obtained an "exact" solution for the conductivity of randomly distributed and non-interacting homogeneous spheres in a homogeneous continuous medium:

$$k_e = k_c \left[\frac{k_d + 2k_c + 2\phi(k_d - k_c)}{k_d + 2k_c - \phi(k_d - k_c)} \right] \qquad (26)$$

Norton Empirical Model (64)

Norton's techniques were based upon the following assumption. The polymer matrix which makes up the foam network is so complex that it would be impossible to model the conductive and radiative energy transfer within the foam. The thermal conductivity of a polymer foam with a known gas content is experimentally measured. Subtracting the thermal conductivity of the gas assuming it had the same total volume would give the "effective" conductivity of the polymer for that particular structure and density.

$$k_{eff_{polymer}} = k_{measured} - k_{gas}$$

The thermal conductivity of the foam with a different gas is then assumed to be

$$k_{foam} = k_{eff_{polymer}} + k_{gas} \qquad (27)$$

Peterson and Hermans Semi-Theoretical Model (67)

Peterson and Hermans derived a general theory for the dielectric constants of a dilute suspension of spheres in a continuum. By direct analogy between heat transfer and electrostatics.

$$k_e = k_c[1 + 3\gamma\phi + 3\gamma^2$$
$$\left(1 + \frac{\gamma}{4} + \frac{\gamma^2}{256} + \ldots \right)\phi^2 + \ldots] \qquad (28)$$

where

$$\gamma = \frac{k_d - k_c}{2k_c + k_d}$$

Progelhof and Throne Empirical Model (70)

By curve fitting the experimental data for several foamed plastics they found that the following empirical equation fit the data best:

$$k_e = k_d \left[1 + A \left(\frac{\rho}{\rho_o} \right)^B \right] \qquad (29)$$

where

$$A = \frac{k_c}{k_d}$$

and B is an empirical constant.

Ratcliffe Empirical Model (71)

Starting with a geometric mean correlation:

$$k_e = k_c^\phi k_d^{(1-\phi)}$$

Ratcliffe analyzed approximately 150 sets of data and determined the variation of the individual data points with the correlation. Based on a mean variation effect he prepared a chart defining probable limits (upper and lower) to the effective thermal conductivity of the two phase medium. Based upon these results he presented a nomograph for predicting effective thermal conductivity.

Russell Theoretical Model (75)

Assuming the pores are cubes of the same size and the isothermal lines are planes, Russell obtained the conductivity using a series parallel network:

$$k_e = k_c \left[\frac{\phi^{2/3} + \frac{k_c}{k_d}(1 - \phi^{2/3})}{\phi^{2/3} - \phi + \frac{k_c}{k_d}(1 + \phi - \phi^{2/3})} \right] \qquad (30)$$

Springer and Tsai Semi-Theoretical Model (78)

The thermal conductivity of a composite with unidirectional filaments in the direction along the filaments (parallel model)

$$k_e = k_c \left[\phi \frac{k_d}{k_c} + (1 - \phi) \right]$$

In the direction normal to the filament an analogy between the response of an unidirectional composite to longitudinal shear loading and heat transfer results in:

$$k_e = k_c \left[\left(1 - \frac{s}{2b} \right) + \frac{a}{b} \int_0^s \frac{dy}{(2a - h) + \frac{k_c}{k_d}} \right]$$

where s = maximum transverse dimension of filament, h = width of the filament, and a, b = dimensions of elemental volume in which filament is mounted.

For a square filament in a square array:

$$k_e = k_c \left[(1 - \sqrt{\phi}) + \frac{1}{\sqrt{\frac{1}{\phi} + \frac{B}{2}}} \right] \qquad (31)$$

and cylindrical filaments in a square array:

$$k_e = k_c \left(1 - 2\sqrt{\frac{\phi}{\pi}} + \frac{1}{B} \left[\pi - \frac{4}{\sqrt{1 - \left(\frac{B^2\phi}{\pi} \right)}} \mathrm{Tan}^{-1} \frac{\sqrt{1 - \frac{B^2\phi}{\pi}}}{1 + \sqrt{\frac{B^2\phi}{\pi}}} \right] \right) \qquad (32)$$

where

$$B = 2 \left(\frac{k_c}{k_d} - 1 \right)$$

Topper Theoretical Model (81)

Using a series-parallel energy model for a system of *cubic* voids in orderly array, the equivalent thermal conductivity was found to be:

$$\frac{1}{k_e} = \left[\frac{1 - \phi^{1/3}}{k_c} + \frac{\phi^{1/3}}{k_d\phi^{2/3} + k_c(1 - \phi^{2/3})} \right] \qquad (33)$$

For *spheres* distributed in a simple cubic lattice:

$$\frac{1}{k_e} = \left[\frac{1 - 2\left[\frac{3\phi}{4\pi}\right]^{1/3}}{k_c} + \frac{\mathrm{Tan}^{-1}\left\{ \frac{\left[\frac{3\phi}{4\pi}\right]^{1/3}}{\left[\frac{k_c}{\pi(k_c - k_d)} - \left[\frac{3\phi}{4\pi}\right]^{2/3}\right]^{1/2}} \right\}}{\pi(k_c - k_d)\left\{ \frac{k_c}{\pi(k_c - k_d)} - \left[\frac{3\phi}{4\pi}\right]^{2/3} \right\}^{1/2}} \right] \qquad (34)$$

Radiant energy transfer has been neglected in this model.

Tsao Theoretical Model (83)

Tsao's model is based on determining a one dimensional porosity, P_1, and the mean, μ, and standard deviation, σ, which relate P_1 to the "two dimensional" or planar porosity, P_2. The bulk porosity, ϕ, is the product of $P_1 \times P_2$. Using a probablistic model Tsao developed a relationship between P_1 and P_2. Using a parallel conductive model the equivalent thermal conductivity is given by the following integral equation:

$$k_c = \frac{1}{\int_0^1 \frac{dP_1}{k_c + (k_d - k_c)\int_{P_1}^1 \frac{1}{\sigma\sqrt{2\pi}} e^{-1/2 \left[\frac{P_1-\mu}{\sigma}\right]^2} dP_1}} \qquad (35)$$

To evaluate this integral the relationship between P_1, μ, and σ must be known.

GENERAL DISCUSSION

The general discussion on the appliability of the theoretical/empirical models presented in the preceding section has been divided into two parts. The first part deals with solid-solid compositions and the second with gas-solid composites. To evaluate the various models presented in the previous section, it is necessary to obtain reliable experimental data. In order that data be acceptable, they must satisfy several important criteria.

First, the experimenter must have described in detail a suitable technique or method for preparing test specimens. Second, the data must be of sufficient size and range of the concentrations to be useful for evaluation at both ends of the discontinuous phase concentration and must have included values of the continuous phase alone. And most important, a reliable, reproducible experimental technique and test set-up must have been used to measure the thermal conductivity of the materials. Much of the available experimental data given in the literature unfortunately do not meet any or all of these criteria. This does not mean that the experimental values not used in this analysis are incorrect, only that they are not acceptable for the purpose of evaluating the accuracy of the various theoretical models.

Solid-Solid Compositions

For a two component mixture the authors have selected the data of Sundstrom & Lee (80) for 62-88 micron glass spheres and 62-125 micron magnesium oxide powder in polyethylene. These experimental data, shown in *Figs. 1* and *2*, were chosen by the authors since the range of filler to matrix conductivity ratio varied from 3 for glass to 164 for magnesium oxide. Measurements were made for filler contents of from zero to 30 percent in 5 percent increments. Also shown in the figures are the theoretically predicted variations of thermal conductivity by the following models:

1. Bruggemen: *Eq 8*
2. Cheng & Vachon: *Eqs 10* and *11*
3. Jefferson, Witzell & Sibbitt: *Eqs 22* and *23*
4. Lewis & Nielsen: *Eq 24*
5. Maxwell: *Eq 26*
6. Russell: *Eq 30*

The theoretical values predicted by the Lewis and Nielsen model are based on $\phi_m = 0.637$, $A_{glass} = 1.5$, and $A_{M_0} = 3.0$. Many of the other models reviewed in the Literature Review section were not plotted since these models reduce to the Maxwellian model when the particles are spherical in shape.

After careful examination of curves for all fillers (79, 80) over the complete range of fillers and additional data of a limited scope (11, 28, 71, 76), it is the author's conclusion that the Lewis and Nielson correlation fits the data best for the range of fillers tested.

For a two component composite of highly non-spherical particles, such as glass filaments, we have been unable to obtain reliable data for direct comparison with the various theoretical models. The majority of models found in the literature for circular or elliptical fibers were derived for specific geometries and spacings of the filaments. The correlation of Lewis and Nielsen does account for filament size, orientation, etc. However, the data we evaluated as reported by Ashton *et al.* (2) and Segal (76) did not accurately describe the specimen preparation for the thermal conductivity measurement system. Nielsen presented an analysis of the Ashton *et al.* data and showed that for the possible range of variables of the physical system his correlation would represent the data.
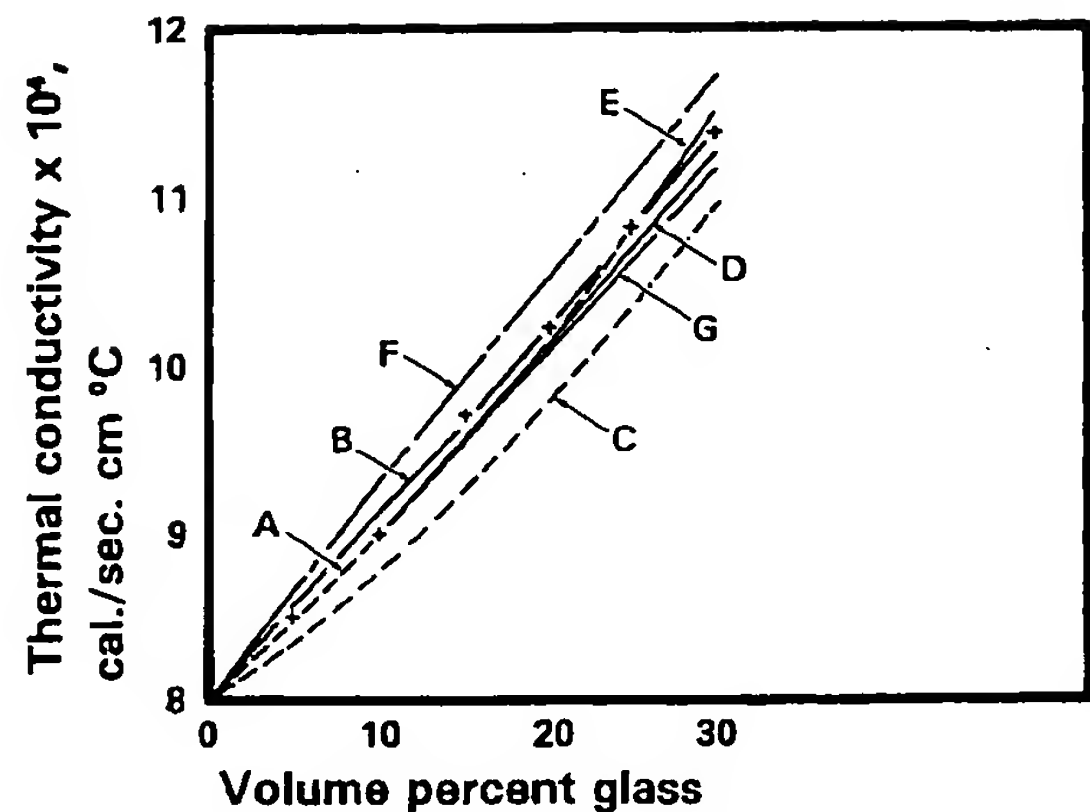

Fig. 1. Glass filled polyethylene. A. Bruggman, B. Cheng & Vachon, C. Jefferson et al., D. Maxwell, E. Lewis & Nielsen, F. Peterson & Hermans, and G. Russell.
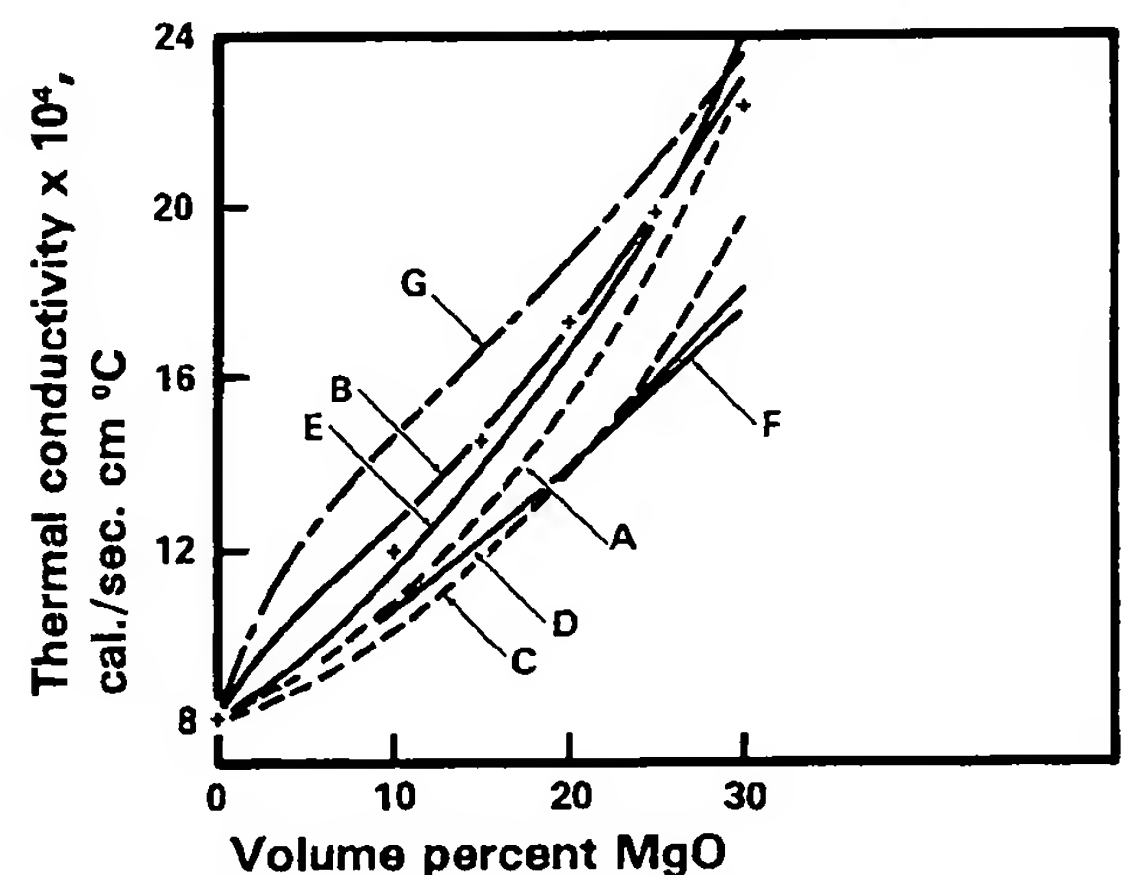

Fig. 2. Magnesium oxide filled polyethylene. A. Bruggman, B. Cheng & Vachon, C. Jefferson et al., D. Maxwell, E. Lewis & Nielsen, F. Peterson & Hermans, and G. Russell.

A more difficult and perplexing problem is the estimation of the thermal conductivity of a composite of a mixture of fillers. This system is encountered in many practical applications. Most likely, one of the fillers would be rod shaped in geometry for strengthening. Two correlations reviewed by the authors for multi-phase composites are those of Budiansky (9) and Hamilton (29). Budiansky's model assumes that the particles are near spherical in shape. Hamilton's model uses a sphericity function to account for non-spherical particles. However, there is no orientation effect. Limiting discussion to near spherical particles, specifically to glass spheres and MgO powder, the authors predict the thermal conductivity of filled polyethylene by Budiansky's, Hamilton's and Lewis & Nielsen's models. In the Hamilton model the sphericity of the glass spheres is assumed to be 1.0, and the MgO powder is assumed to be 0.625. Since the Lewis and Nielsen correlation is for a two component composite mixture, the three component mixture was estimated by first determining the conductivity of the polymer and one filler and then the conductivity of the mixture with the third filler. Results

were obtained for the fillers being added in different sequences. The results are listed in *Table 1*. Based upon these results, it is apparent that the order of filler addition when using the Lewis and Nielsen model has little effect. The results obtained by Budiansky's model are in fair agreement with the Lewis and Nielsen model but both significantly underestimate the composite conductivity. Owing to the lack of accurate data, the authors are reluctant to recommend any correlation.

In predicting the thermal conductivity of any two or multi phase mixture by one of the theoretical or empirical relations discussed in this paper, it is assumed that good adhesion between the polymer and the filler is present. If there is a thin gas layer between the filler and the polymer, the "effective" thermal conductivity of the particle could be considerably smaller than the thermal conductivity of the pure filler phase. Microphotographs (17, 73) of fractured glass fiber reinforced material indicates that with poor wetting this factor would be appreciable.

Gas-Solid Compositions

In the preceding section the effect of solid additives on the thermal conductivity of a continuous matrix was discussed. The only energy transfer process that occurs within the composite, if complete wetting between the filler and the continuous media is assumed, is conduction. However, the energy transfer process in a gas filled composite is much more complex. Shown in *Fig. 3* is an idealized model of a gas filled composite filling the space between two parallel planes which are at temperatures T_1 and T_2. respectively. The insert is of a single bubble, assumed to be spherical in shape. First assume that the continuous phase is opaque to electromagnetic radiation. This important assumption will be discussed further in our analysis. The only mode of energy transfer in the continuous phase is conduction. If the gas bubbles are relatively small and spaced far apart, the isotherms or lines of constant temperature for steady state condition will be parallel to planes 1 and 2. These isotherms are shown as dotted lines. Thus, the temperature at any point on the surface of the bubbles or in the polymer assuming the thermal conductivity is constant is given by:

Table 1. Thermal Conductivity

MgO content, percent	Glass content, percent		
	0	10	20
0	8.01	1. 8.98	1. 10.13
	1. 11.59	1a. 13.1	1a. 15.0
		b. 13.0	b. 14.6
10%		2. 9.4	2. 10.0
		3. 13.1	3. 15.1
	1. 16.50	1a. 19.0	1a. 22.1
		b. 18.4	b. 20.6
20%		2. 10.28	2. 10.92
		3. 22.6	3. 26.5

1. Lewis & Nielsen
  a. (Polymer & Glass) + MgO
  b. (Polymer & MgO + Glass)
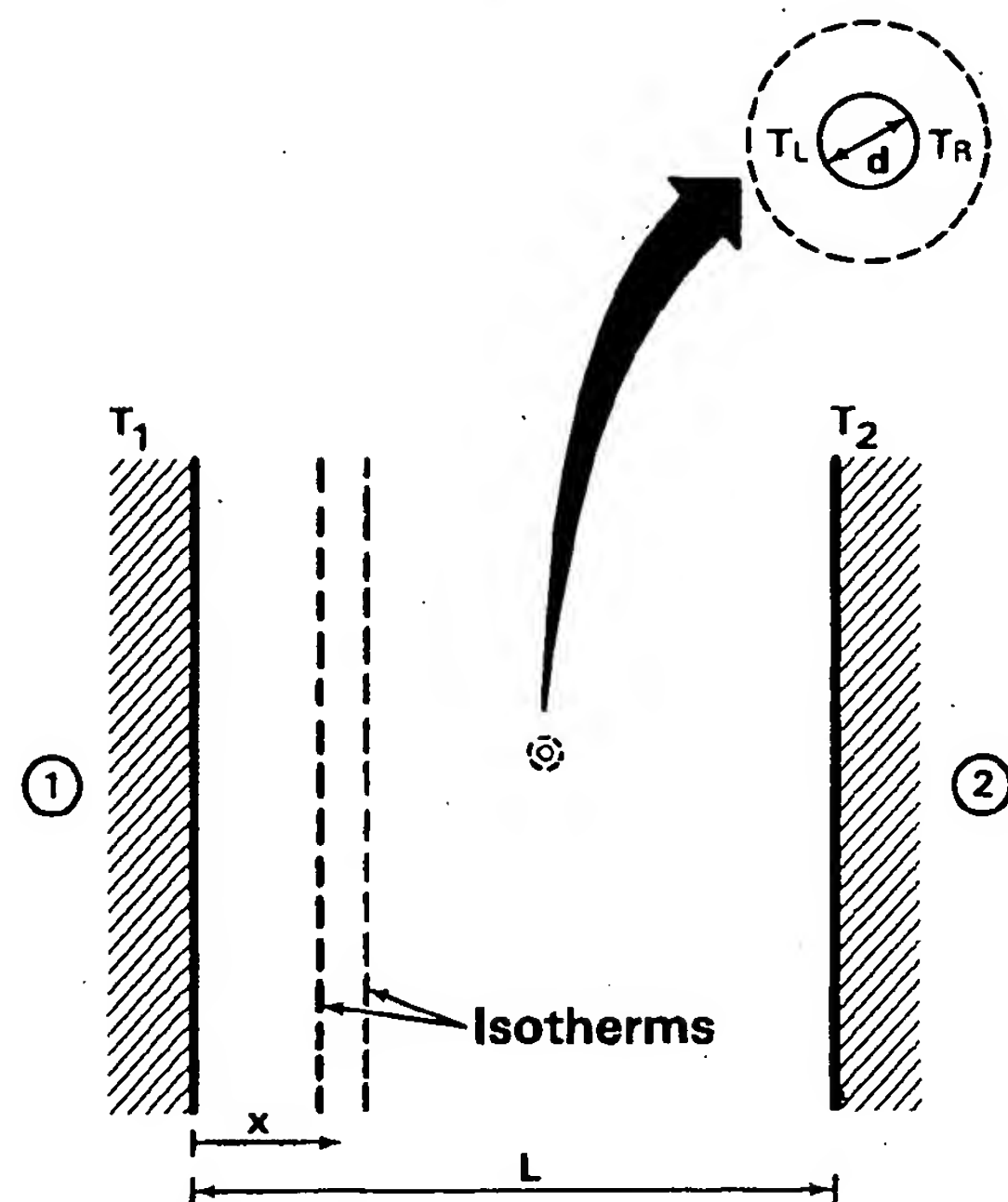2. Hamilton & Crosier
3. Budiansky

Fig. 3. Gas filled polymer.

$$T = T_1 + \frac{T_2 - T_1}{L} x$$

where x is the distance from plane 1. With a linear temperature gradient across the bubble, energy will be transferred by conduction and/or convection inside the bubble and by radiation on the inside surface of the bubble. If the gas molecules within the spherical bubble transfer energy only by molecular action, the rate of energy transfer is governed by Fourier's law:

$$\frac{q}{A} = -k \frac{\partial T}{\partial x}$$

If, however, the energy level (and thus the temperature difference) across the bubble is large, energy transfer will occur by molecular motion as well as by molecular transport (8, 14). The rate of energy transfer is governed by Newton's law of cooling:

$$\frac{q}{A} = h \, (T_a - T_b)$$

where h is the convective conductance and T_a and T_b are the temperature of the surface and the fluid respectively. The molecular motion will result in a microscopic velocity field developing inside of the bubble (13). Thus, the rate of energy transfer will be significantly greater than that which would occur with pure molecular conduction. The development of the internal velocity field which enhances the rate of heat transfer is dependent upon many factors. These include the bubble diameter, temperature gradient, orientation, gas properties, etc. Techniques to correlate the effect of each of these parameters on the rate of energy transfer usually rely on non-dimensional numbers. The common correlation for free convection effects is (7):

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$$\frac{hd}{k} = f\left(\frac{g\rho^2 \beta d^3 \Delta T_b}{\mu^2} \frac{d^3}{L} \Delta T_b\right)$$

Nusselt Number   Grashof-Prandtl Number

where: ρ = gas density, β = coefficient of thermal expansion of the gas, μ = absolute viscosity of the gas, d = bubble diameter, and ΔT_b = temperature difference across the bubble.

Thus, for a given fluid the significant parameters are d^3 and ΔT_b. However, the temperature drop across the bubble is a function of the overall temperature drop' across the foam sheet:

$$T_b = \frac{T_1 - T_2}{L} d$$

Therefore,

$$\frac{hd}{k} = f\left(\frac{g\rho^2 \beta}{\mu^2} \frac{T_1 - T_2}{L} d^4\right)$$

It is apparent that the convective effects are a function of the temperature, gradient, direction of energy flow (horizontal or vertical) and the bubble diameter to the fourth power. The only criterion commonly found in the literature is the bubble diameter. Convective effects are largest for large diameter bubbles. Effective cell or bubble size for relatively low density foams can be found in Table 2 of Guenther's (26) paper. From this table it is evident that cell size is inversely proportionally to foam density. Thus, the convective effects will be greatest in low density foams.

An estimate of the relative magnitude of the energy transfer within a bubble by radiation as compared to that by pure conduction can be made by considering the energy transfer between two parallel planes spaced a distance apart. This geometry is used instead of a sphere in that it can be analyzed theoretically. The planes are assumed to be perfect absorbers and at temperatures T_a and T_b. If T_a and T_b only differ by a temperature difference ϵ, T_a can be rewritten as:

$$T_a = T_b + \epsilon$$

The rate of energy transfer between the two surfaces is described by:

conduction: $\dfrac{q}{A} = \dfrac{k}{d}(T_a - T_b)$

radiation: $\dfrac{q}{A} = \sigma(T_a^4 - T_b^4)$

where σ is the Stephan-Boltzman constant. Since the temperature difference across the surfaces is ϵ the conductances for the two modes of heat transfer are:

$$G_{conduction} = \frac{k\epsilon}{d}$$

$$G_{convection} = 0.6872 \times 10^{-8} T_b^3 \epsilon$$

Shown in Fig. 4 are comparisons using air as the encapsulated gas for various ranges of bubble sizes in many foam applications. Even though these results were derived for a thin air gap between two planes, the relative effects would be similar for a spherical inclusion. Assuming no internal convective currents, the results

clearly indicate that radiation can be a significant portion of the total energy transfer within a cell when the cell size is large, $d = 0.040$ in., and the temperature is high, $T > 200°F$. As was shown in the section on convective effects, the greatest effect will occur in low density foams.

If the energy transfer process in a cell is treated as the sum of convection and radiation, there will be a specific cell size at which the effective thermal conductivity of the foam will reach a minimum and then increase as the foam density is further decreased. This effect is clearly seen in the data of Baxter and Jones (5) for polystyrene, which has been replotted in Fig. 5. The minimum thermal conductivity, 0.0173 Btu/hr ft°F, occurs at foam densities of from 2-8 lb/cu ft. It is also apparent that foams will exhibit significantly different thermal properties depending upon the direction of foam rise. In effect the cells will not be true spheres but will be ellipsoidal in shape. The convective effects in the direction of the major axis of the inclusion will be greater than that in the direction of the minor axis. Since the direction of rise is the same as the major axis the effective thermal conductivity in the direction of rise will be greater than that of the transverse direction. In addition, if the foam is an open cell geometry, the air may migrate from cell to cell forming a natural convection pattern within the foam body.
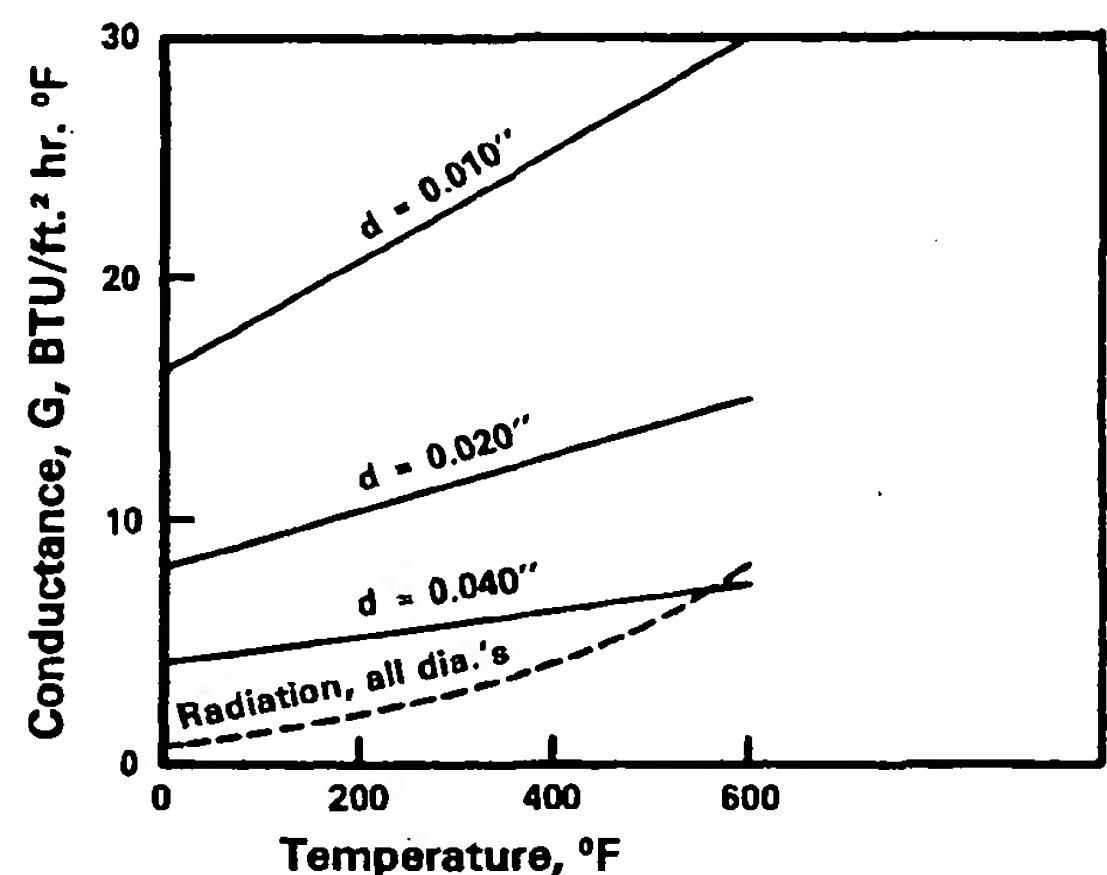

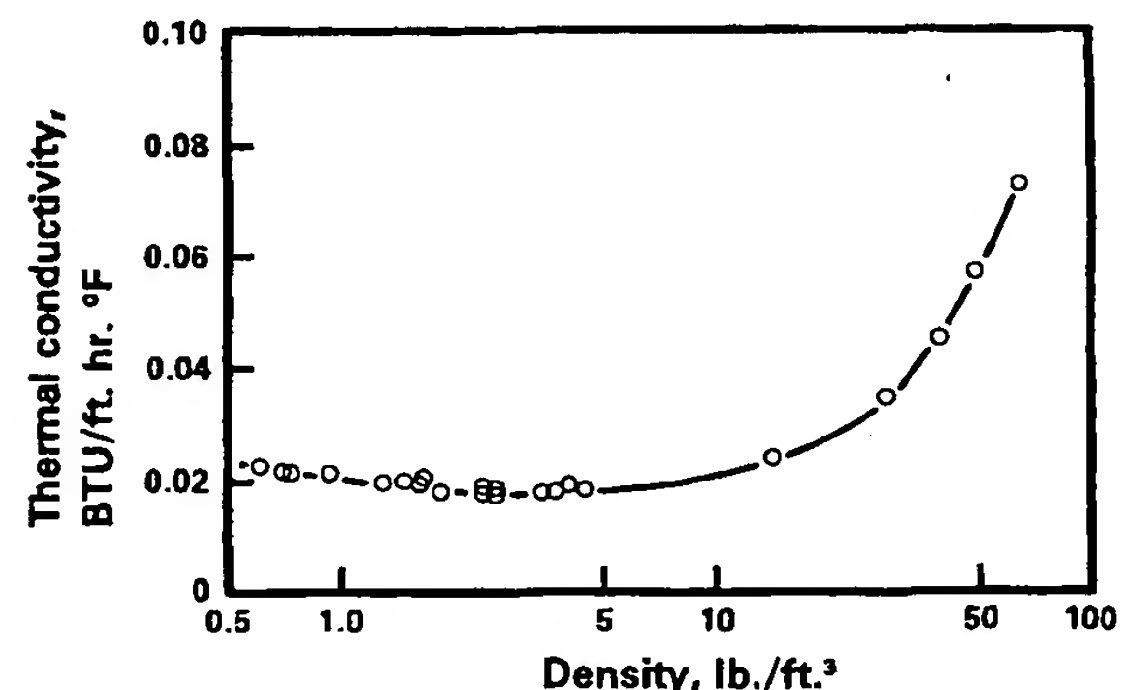Fig. 4. Conduction/radiation effects.

Fig. 5. Thermal conductivity of polystyrene foam.

One of the original assumptions made in the analysis of the energy transfer process in a gas filled composite was that the continuous phase does not transmit electromagnetic radiation. However, this assumption is not valid for polymers over all conditions. The characteristic property that identifies the degree of transparency of a material is the absorption coefficient, α, which is defined in the following manner:

$$dI(\lambda) = -\alpha(\lambda) I(\lambda) dx$$

where: I = incident energy beam, λ = wave length, and x = distance. As α decreases in value, the transmittance of radiant energy through a sheet of given thickness increases. If α is zero at a given wave length, the sheet is totally transparent, regardless of sheet thickness. Normally for a given material the absorption coefficient is a highly irregular function of wavelength. This is seen in *Fig. 6*. Also shown in the figure is an approximation of the irregular curve by a step function curve. The data presented in *Fig. 6* were obtained from sheet specimens. Results for thin films can be significantly different than those for a sheet. The apparent discrepancy occurs when the wave length of the incident radiation is of the same order of magnitude as the film thickness. Additional unpublished data for nylon-6 and polyethylene sheets indicate that crystalline polymers are stronger absorbers than noncrystalline polymers. However, most polymeric materials do transmit some radiant energy. It is necessary to determine the rate of transmission for various materials, however.

The simplest model to describe the transmission of radiant energy through an absorbing-scattering media is the "two flux" or one-dimensional model. A comprehensive discussion of this technique can be found in references (30, 69, 74). Estimating the rate of energy transfer in a scattering absorbing medium is extremely complex and is a function of the type of inclusion, polymer, radiation spectrum, etc. It can be that there is no scattering and if the temperatures of the polymer and the source are low, (e.g., less than 200°F) and if the foam cell walls have absorption characteristics shown in *Fig. 6*. The results of Harding and James (31) indicate that a low density polystyrene foam may have a wall thickness of only 40 molecules thick. This thickness apparently is a lower limit to differentiating between a film and a sheet. This conclusion is supported by the data of Chute, Walker and DeWitz on the radiant heating of low density polystyrene foam indicating that their material was relatively opaque to long wavelength radiation but considerably transparent to short or high temperature radiation.

Most of the theoretical models listed in the beginning of the report are based on a specific thermal conductivity of the discrete phase of the composite. From our discussion it is apparent that this idealization is not representative of many low density foams and application of these models would result in erroneous predictions. Each polymer, gas, application, etc. must be considered before attempting to estimate the thermal conductivity of the foam. For this reason the approach of Harding (32-36), based on a semi-empirical approach, shows consid-
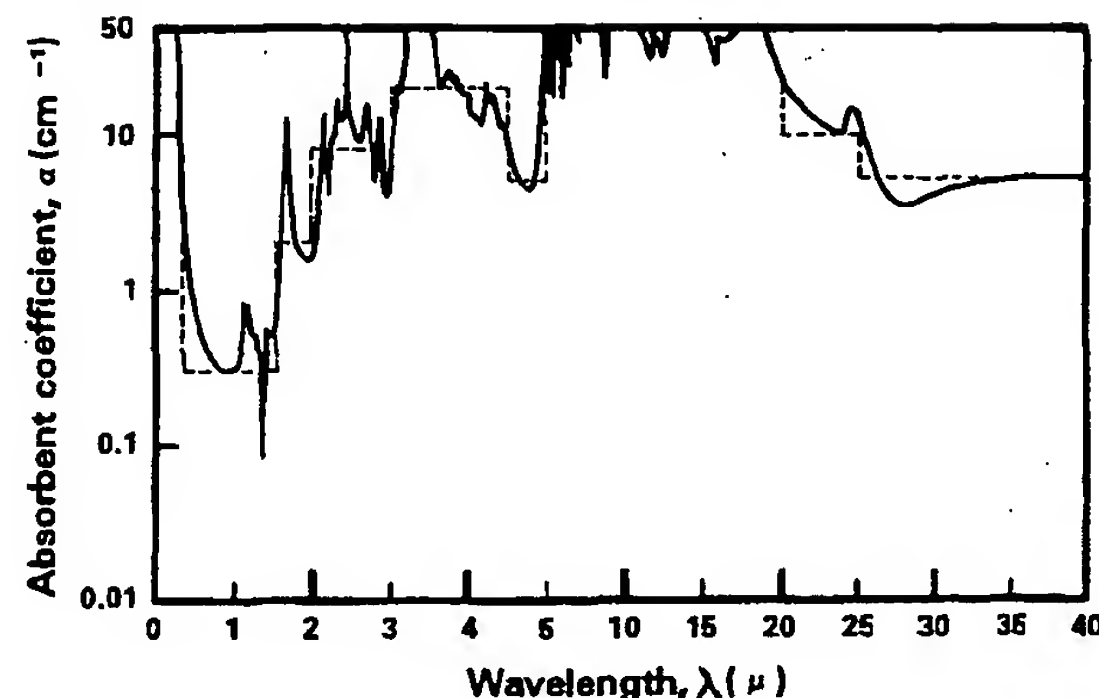

Fig. 6. Absorption characteristics of polystyrene.

erable merit. However, for each polymer, configuration, and environmental condition the empirical constants should be evaluated. For example, if empirical coefficients were measured for an effective thermal conductivity of polystyrene in a room temperature environment, the application of these coefficients to a radiant heating system would also result in erroneous energy transfer rates.

In our discussions we have based our assumptions that the properties of the encapsulated gas are known. However, when foams are blown with gases other than air there is an aging effect (16, 18, 19, 36, 42, 52). This is due to the diffusion of blowing gas out of the foam and air into the foam. Recently models have been proposed to account for the diffusion process. The models usually assume that the cells are cubic and the gas diffuses through a series of sheets. This model appears to be satisfactory for low density foams but may not be applicable for higher density regions, such as the skin of a structural foam.

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